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Poly(carboxylate) cement pack contg. silicate cpds. - used in dentistry, orthopaedic surgery and as grouting cements

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A poly(carboxylate) cement pack comprises (a) a naturally-occurring orthosilicate, pyrosilicate, cyclic or chain silicate comprising recurring metasilicate units, or aluminosilicate having a Al:Si molar ratio $\geq$ 2:3, or a blast furnace slag, and (b) a water-soluble poly(carboxylic acid) or a precursor thereof. The two ingredients are mixed with water to give a mass that remains plastic long enough to be formed into the desired shape prior to hardening to a cement.

USE/ADVANTAGES

For dentistry, orthopaedic surgery and grouting cements, and esp. for cementing in moist environments. The ingredients are relatively cheap.

DETAIL

(a) is e.g. willemite, hemimorphite, sodalite, spurrite, gehlenite, larnite, wollastonite, nepheline, levynite, aphrosiderite, hackmanite, scolecite, thuringite or danalite. Alternatively, (a) is a by-product from the smelting of Cu, Zn, Pb or Fe. Cpd. (a) pref. passes through a 150 mesh, esp. 350 mesh B.S. sieve, and $>$ 1 cpd. (a) can be used.

(b) is pref. acrylic acid homopolymer or a copolymer of acrylic acid or itaconic acid, or precursors thereof. The comonomer is e.g. acrylamide or acrylonitrile. The precursor is e.g. a poly (carboxylic acid anhydride), e.g. poly(maleic anhydride), opt. copolymerised with ethylene, butene, propene or styrene. (ii) is pref. linear, with an average mol. wt. of 1000-100,000 (esp. 10,000-25000).

(b) is pref. present as a 20-65 wt.% aq. soln. The pack pref. contains 15-85 wt.% (a), 3-50 wt.% (b) and 5-70 wt.% water. A two-part pack can be used, one part contg. powder and the other part liq., the powder:liq. wt. ratio pref. being from 0.5:1 to 5:1. There is pref. 1-10 pts. wt. of (a) per pt. wt. of (b).

EXAMPLE

A 49.5 wt.% aq. soln. of a styrene-maleic acid anhydride copolymer (mol. wt. 1,600) was mixed, in turn, with powdered willemite, hemimorphite, sodalite and spurrite (each of particle size $<$ 37 μm). In each case, some soln. was spatulated onto a glass block, with the maximum amt. of powdered silicate material which allowed a smooth homogeneous mix to be formed. The mix was left to harden for $\geq$ 24 hrs. In each case there was obtd. a hydrolytically-stable hard cement. (5p

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PATENT SPECIFICATION

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(54) POLY(CARBOXYLATE) CEMENTS

(71) We, NATIONAL RESEARCH DEVELOPMENT CORPORATION, a British Corporation established by Statute, of Kingsgate House, 66—74 Victoria Street, London, S.W.1., do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to packs for use in, and a process for, the preparation of poly(carboxylate) cements.

Poly(carboxylate) cements are formed by the reaction of a poly(carboxylic acid) and an ion-leachable inorganic compound. The preparation of such cements is described and claimed in British Patent No. 1,139,430, in which the inorganic compound used is zinc oxide, and in British Patent No. 1,316,129, in which the inorganic compound used is a fluoroaluminosilicate glass. Poly(carboxylate) cements were originally developed primarily for dental and surgical applications in which the appearance of the cement is very important and in the preparation of which the use of starting materials of high purity is necessary. In a number of other applications, however, the appearance of the cement and the purity of the starting materials are of less significance than the cost of the starting materials, and for these applications it would be desirable to be able to prepare poly(carboxylate) cements from relatively inexpensive starting materials.

In one aspect, the present invention provides a poly(carboxylate) cement pack which comprises

(i) a naturally-occurring orthosilicate, pyrosilicate, cyclic or chain silicate comprising recurring metasilicate units, or aluminosilicate having a Al:Si molar ratio greater than 2:3; or a blast furnace slag; and

(ii) a water-soluble poly(carboxylic acid) or a precursor thereof (as herein defined)

In another aspect, the present invention provides a process for the preparation of a poly(carboxylate) cement which comprises mixing a naturally-occurring orthosilicate, pyrosilicate, cyclic or chain silicate comprising recurring metasilicate units, or aluminosilicate having a Al:Si molar ratio greater than 2:3; or a blast furnace slag with a water-soluble poly(carboxylic acid) or a precursor thereof (as herein defined) in the presence of water to give a mass that remains plastic long enough to be formed into a desired shape prior to hardening as a poly(carboxylate) cement.

The invention also provides a poly(carboxylate) cement whenever produced by the process according to the present invention. Examples of materials (i) suitable for use in the present invention include willemite, hemimorphite, sodalite, spurrite, gehlenite, larnite, wollastonite, nepheline, levynite, aphrosiderite, hackmanite, scolecite, thuringite and danalite.

Particularly preferred blast furnace slags are those obtained as by-products in metal smelting processes, especially those obtained in the smelting of copper, zinc, lead and iron. These latter materials are acid-decomposable complex silicates containing small quantities of copper, zinc, lead or iron, and may readily be obtained from various metal smelting plants. Being by-products of metal smelting processes these slags are relatively inexpensive.

The materials (i) used in the present invention may be readily obtained in fine powder form. The degree of fineness of the powder should preferably be such that

when mixed with poly(carboxylic acid) or precursor thereof in the presence of water, a smooth cement paste which sets within an acceptable period is produced. The degree of fineness of the powder preferably is such that it will pass through a 150 mesh B.S. sieve and most preferably is such that it will pass through a 350 mesh B.S. sieve. Mixtures of two or more of the materials (i) may be used if desired.

The preferred poly(carboxylic acid)s and precursors thereof are those prepared by homopolymerisation and copolymerisation of unsaturated aliphatic carboxylic acids, for example acrylic acid, itaconic acid, mesaconic acid, citraconic acid and aconitic acid, and copolymerisation of these acids with other unsaturated aliphatic monomers, for example acrylamide and acrylonitrile. Particularly preferred are homopolymers of acrylic acid and copolymers of acrylic acid, especially copolymers of acrylic acid and itaconic acid. Alternatively, it is possible to use a poly(carboxylic acid) precursor by which term is meant a polymeric material which is convertible by action of water to poly(carboxylic acid) for example a poly(carboxylic acid anhydride) or other suitable polymer. The poly(carboxylic acid anhydride) may be a homopolymer of an unsaturated carboxylic acid anhydride, or a copolymer of such anhydride with a vinyl monomer, particularly a vinyl hydrocarbon monomer. Particularly good results may be obtained using homopolymers of maleic anhydride and copolymers of maleic anhydride with ethylene, propene, butene and styrene.

The poly(carboxylic acid) or precursor thereof is preferably linear, although branched polymers may also be used, and has an average molecular weight preferably of from 1000 to 100,000 and most preferably of from 10,000 to 25,000. In this specification, unless otherwise indicated, the average molecular weight is that measured by an absolute method such as light scattering or ultracentrifuge sedimentation.

Examples of suitable combinations of materials (i) and poly(carboxylic acids) or precursors thereof are willemite/polyacrylic acid, willemite/polymethacrylic acid, danalite/polymethacrylic acid, hemimorphite/polymethacrylic acid, hemimorphite/styrene-maleic anhydride copolymers, sodalite/styrene-maleic anhydride copolymer, spurrite/styrene-maleic anhydride copolymer, willemite/styrene-maleic anhydride copolymer, hemimorphite/ethylene-maleic anhydride copolymers, and willemite/ethylene-maleic anhydride copolymer.

In the pack, and when used in the process, according to the present invention, it is preferred that the poly(carboxylic acid) or precursor thereof is in the form of an aqueous solution of which from 20 to 65% by weight is constituted by poly(carboxylic acid) or precursor thereof.

In the pack, it is preferred that from 15 to 85% by weight is constituted by the material (i) from 3 to 50% by weight is constituted by the poly(carboxylic acid) or precursor thereof and from 5 to 70% by weight is constituted by water.

The pack may be a two-part pack in which the contents of one part are powder and the contents of the other part are liquid, the powder and the liquid being in separate containers. The powder:liquid weight ratio in the two parts is preferably from 0.5:1 to 5:1 so that when the entire contents of the pack are mixed together a rapidly hardening cement is obtained. Alternatively, both the powder and the liquid may be encapsulated in the same capsule, in a desired ratio, provided that physical means are present to prevent premature reaction.

The cement may be made in conventional manner. Thus, the powder and the liquid in the pack are brought together and mixed to form a plastic mass which can be cast, moulded or otherwise formed into the required shape during the brief period in which the plastic mass retains its plastic properties. The components can be mixed quite rapidly to give a uniform mass which commences to harden in a few minutes and is usually set within ten minutes of mixing. The rate of hardening and strength of the final product are partly determined by the powder:liquid ratio which is preferably as high as possible compatible with adequate working time. The optimum ratio for a particular combination of material (i) and poly(carboxylic acid) or precursor thereof may be determined readily by preliminary experiments. Too little or too much powder normally results in a mixture that is more difficult to form into a desired shape. Particularly good results have been obtained using from 1 to 10 parts by weight of silicate mineral for each part by weight of poly(carboxylic acid) or precursor thereof.

Certain of the poly(carboxylate) cements prepared from the pack or by the process according to the present invention find application in dentistry and also in orthopaedic surgery where they may be used to assist in the re-setting of fractured

bone material. They also find application as grouting cements and are particularly useful for cementing in moist environments.

The invention is illustrated by the following Examples:

EXAMPLE 1.

This Example describes the production of poly(carboxylate) cements from various combinations of naturally-occuring acid-decomposable silicate minerals and poly(carboxylic acid)s or precursor thereof.

The following silicate minerals were obtained in the form of powder having a particle size of less than 37 μm: willemite, hemimorphite, danalite, sodalite and spurrite. Poly(carboxylic acid) solutions were made up as follows:

Polyacrylic acid	molecular weight 23,000 47.6% by weight aqueous solution
Polymethacrylic acid	molecular weight approx. 26,000 20% by weight aqueous solution (Versicol K13 from Allied Colloids Ltd., Bradford ("VERSICOL" is a registered Trade Mark)
Styrene-maleic acid anhydride copolymer	molecular weight approx. 1,600 49.5% by weight aqueous solution (from Monsanto styrene-maleic anhydride copolymer powder)
Ethylene-maleic acid anhydride copolymer	25% by weight aqueous solution (Monsanto 21)

The molecular weight of the polyacrylic acid was estimated from viscosity measurements made at 25°C using a 1% w/v solution in 2 M sodium hydroxide; the solution had a relative viscosity of 1.37. The viscosity of a 2% aqueous solution of the ethylene-maleic acid anhydride copolymer was 5 cps as measured using a Brookfield R.V.T. Rotational Viscometer at 10 revs per minute.

The silicate minerals and the poly(carboxylic acid) solutions were mixed in various combinations as indicated by the symbol X in Table 1. In each case, a quantity of solution was spatulated, on a glass block, with the maximum quantity of powdered silicate mineral which allowed a smooth homogeneous mix to be formed. The resulting mix was then allowed to harden for at least 24 hours.

TABLE 1.

Mineral	Polyacrylic acid	Styrene-maleic acid anhydride copolymer	Ethylene-maleic acid anhydride copolymer	Polymethacrylic acid
Willemite	X	X	X	X
Hemimorphite		X	X	X
Danalite				X
Sodalite		X		
Spurrite		X		

In each case there was obtained a hydrolytically-stable hard cement. The cements obtained using the solution prepared from styrene-maleic acid anhydride copolymer were found to be stable in an equivolume water/acetone mixture.

EXAMPLE 2.

This Example describes the production of poly(carboxylate) cement using blast furnace slag.

Blast furnace slags from the smelting of copper, zinc, lead and iron obtained

from various manufacturers were dried, ground if necessary, and sieved to a particle size of less than 45 μm. Each powder produced was mixed with a 50% by weight aqueous solution of polyacrylic acid having a molecular weight of 23,000 in a powder to liquid ratio P/L as shown in Table 2. Each resulting mixture was allowed to cure in a mould for 1 hour and the compressive strength of the resulting product was measured (A) after immersion in water for 23 hours or (B) after immersion in liquid paraffin for 23 hours or (C) after immersion in liquid paraffin for 23 hours followed by immersion in water for 24 hours, as indicated in Table 2. The results for compressive strength are given in Table 2.

TABLE 2.

Slag	P/L (gml^{-1})	Compressive Strength (Nmm^{-2})	Preparation Method
Zn	1.5	0.2	A
Pb	2.0	0.5	A
Cu	1.5	1.9	A
Cu	1.5	0.4	A
Cu	3.0	23	B
Cu	3.0	9.0	C
Fe	1.0	4.8	A
Fe	1.0	1.8	A

WHAT WE CLAIM IS:—

1. A poly(carboxylate) cement pack which comprises (i) a naturally-occurring orthosilicate, pyrosilicate, cyclic or chain silicate comprising recurring metasilicate units, or aluminosilicate having a Al:Si molar ratio greater than 2:3; or a blast furnace slag and (ii) a water-soluble poly(carboxylic acid) or a precursor thereof (as herein defined).

2. A poly(carboxylate) cement pack according to Claim 1 in which (i) comprises willemite, hemimorphite, sodalite, spurrite, gehlenite, larnite, wollastonite, nepheline, levynite, aphrosiderite, hackmanite, scolecite, thuringite or danalite.

3. A poly(carboxylate) cement pack according to Claim 1, in which (i) comprises blast furnace slag.

4. A poly(carboxylate) cement pack according to Claim 3, in which the blast furnace slag has been obtained from the smelting of copper, zinc, lead or iron.

5. A poly(carboxylate) cement pack according to any of the preceding claims, in which the degree of fineness of (i) is such that it will pass through a 150 mesh B.S. sieve.

6. A poly(carboxylate) cement pack according to any of the preceding claims, in which the poly(carboxylic acid) comprises a homopolymer or copolymer of acrylic acid or a precursor thereof.

7. A poly(carboxylate) cement pack according to Claim 6, in which the poly(carboxylic acid) comprises a copolymer of acrylic acid and itaconic acid or a precursor thereof.

8. A poly(carboxylate) cement pack according to any of the preceding claims, in which the poly(carboxylic acid) precursor comprises a poly(carboxylic acid anhydride).

9. A poly(carboxylate) cement pack according to any of the preceding claims, in which the poly(carboxylic acid) or precursor thereof has an average molecular weight of from 1000 to 100,000.

10. A poly(carboxylate) cement pack according to any of the preceding claims, in which the poly(carboxylic acid) or precursor thereof is in the form of an aqueous solution of which from 20 to 65% by weight is constituted by poly(carboxylic acid) or precursor thereof.

11. A poly(carboxylate) cement pack according to any of the preceding claims, in which from 15 to 85% by weight is constituted by (i) from 3 to 50% by weight is constituted by the poly(carboxylic acid) or precursor thereof, and from 5 to 70% by weight is constituted by water.

12. A poly(carboxylate) cement pack substantially as hereinbefore described.

13. A process for the preparation of a poly(carboxylate) cement which comprises mixing (i) a naturally-occuring orthosilicate, pyrosilicate, cyclic or chain silicate comprising recurring metasilicate units, or aluminosilicate having a Al:Si molar ratio greater than 2:3; or a blast furnace slag, (ii) a water-soluble poly(carboxylic acid) or a precursor thereof (as herein defined) in the presence of water to give a mass that remains plastic long enough to be formed into a desired shape prior to hardening as a poly(carboxylate) cement.

14. A process according to Claim 13, in which (i) comprises willemite, hemimorphite, sodalite, spurrite, gehlenite, larnite, wollastonite, nepheline, levynite, aphrosiderite, hackmanite, scolecite, thuringite or danalite.

15. A process according to Claim 13, in which (i) comprises blast furnace slag.

16. A process according to Claim 15, in which the blast furnace slag has been obtained from the smelting of copper, zinc, lead or iron.

17. A process according to any of Claims 13 to 16, in which the degree of fineness of (i) is such that it will pass through a 150 mesh B.S. sieve.

18. A process according to any of Claims 13 to 17, in which the poly(carboxylic acid) comprises a homopolymer or copolymer of acrylic acid or a precursor thereof.

19. A process according to Claim 18, in which the poly(carboxylic acid) comprises a copolymer of acrylic acid and itaconic acid or a precursor thereof.

20. A process according to Claims 13 to 19, in which the poly(carboxylic acid) precursor comprises a poly(carboxylic acid anhydride).

21. A process according to any of Claims 13 to 20, in which the poly(carboxylic acid) or precursor thereof has an average molecular weight of from 1000 to 100,000.

22. A process according to any of Claims 13 to 21, in which the poly(carboxylic acid) or precursor thereof is in the form of an aqueous solution of which from 20 to 65% by weight is constituted by poly(carboxylic acid) or precursor thereof.

23. A process according to any of Claims 13 to 22, in which there is used from 1 to 10 parts by weight of (i) for each part by weight of poly(carboxylic acid) or precursor thereof.

24. A process according to any of Claims 13 to 23, substantially as described in the Examples.

25. A poly(carboxylate) cement whenever produced by a process according to any of Claims 13 to 24.

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